CHEMICAL CHARACTERIZATION OF AMBIENT PM_1 PARTICLES AND THEIR HEALTH RISK ASSESSMENT

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INTRODUCTION

Atmospheric aerosols have been studied intensively in recent years as they affect climate (IPCC, 2013) and human health (WHO, 2013). They are usually defined as colloidal system of liquid, and/or solid particles suspended in a gas. The parameters that determine the affect of aerosols on environment and health are concentration, size, structure, chemical composition, etc., (Poschl, 2005). Atmospheric chemical reactions influence the ion composition of aerosol particles. Aerosols also have significant effect on radiative forcing, a slight change in their atmospheric distribution can affect the climate, such effects can also be linked with the changes in the amount of sulphates, nitrate and carbonaceous aerosols induced by natural and anthropogenic activities. Intergovernmental Panel on Climate Change (IPCC) reported that a yearly emission of about 3400 million tons of particulate matter is composed of 15% anthropogenic sources while 85% of it is from natural sources (Olario et al., 2015). Natural sources of atmospheric aerosols include volcanic eruption, sea salt, soil dust suspension, forest fires, etc. Soil dust re-suspension may occur especially during severe dust storm events when large amounts of soil are moved across land and ocean, while anthropogenic sources are transport, industrial activities, fuel combustion, biomass burning, etc., (Pitts and Pitts, 2000, Griffin et al., 2001).

The particle size distribution of aerosols is a key factor in an accurate and reliable assessment of their impact on human health. This is due to their ability to penetrate into respiratory tract, which is a direct function of the aerodynamic diameter of these particles (Kushwaha et al., 2013). The chemical composition of Particulate matter (PM) varies greatly and depends on many factors, such as combustion sources, climate and type of urban and industrial pollution. The chemical composition of Total Suspended Particulate Matter (TSPM), PM_{10} and $PM_{2.5}$ were also studied in different parts of the world and are composed of carbonaceous aerosols (Satsangi et al., 2012, Pachauri et al., 2013), ions (Kulshreshtha et al., 2010, Deshmukh et al., 2012, Zhamsueva et al., 2015), metals (Mishra et al., 2013, Chen and Lippmann, 2009, Haritash and Kaushik, 2007), Polycyclic Aromatic Hydrocarbons (PAHs) (Sharma et al., 2007, Ansari et al., 2010, Jung et al., 2011), etc. In TSP the percentage contribution of Organic carbon (OC) and Elemental Carbon (EC) is 11.8 and 1.5% (Satsangi et al., 2012) and ions contributes to ~30% (Morales et al., 1998)

whereas, in PM_{10} and $PM_{2.5}$ the percent contribution of carbonaceous aerosol is 32-46% (Querol et al., 2008), ions 1.7- 76.9% (Deshmukh et al., 2012), metals 6.2% (Kulshreshtha et al., 2014) and PAHs contributes 10% of total mass (Ravindra et al., 2001).

TSP, PM_{10} and $PM_{2.5}$ are composed of carbonaceous aerosols: Organic Carbon and Elemental Carbon (OC and EC) or Black carbon BC (soot). Although, the EC and BC are emitted from the same sources, they differ from each other in their physical, chemical and optical properties. Black carbon is emitted from various sources which are mostly primary in origin. For instance, in the lower troposphere, the major emission sources of BC are fossil fuel and biomass burning at the surface. Aircraft engine exhaust is a source of BC in the upper troposphere and lower stratosphere (Safai et al., 2012). Organic carbon is emitted from both primary and secondary sources. The secondary source of organic carbon is essentially the condensation of low vapour pressure compounds which are emitted as primary pollutants or formed in the atmosphere (Sandrini et al., 2014). Recent studies also support that OC emitted during biomass burning also contain a small component of humic like substances (HULIS) and brown carbon, which absorbs radiation at shorter wavelengths (Ram and Sarin, 2015). Organic fraction of atmospheric particulate matter is most difficult to characterize due to the variability in the chemical composition, sources and possible chemical transformations within the atmosphere. Airborne particulate matter contains (PAHs) which makes them very harmful for human health. Among all of the PAHs, Benzo (α) pyrene (BaP) is a well-studied five-ring carbon. It is particularly important for the environmental toxicology as one of the most mutagenic and carcinogenic hydrocarbon (Kozielska et al., 2015). PAHs are formed during incomplete combustion of fossil fuels, biomass or other organic substances like tobacco or food. In urban areas, a large amount of PAHs are derived from incomplete combustion in motor vehicle engines, especially heavy-duty trucks and diesel engines. PAHs exist in atmosphere in both vapor and particulate phase (Dubey et al., 2015). PAHs in air exhibits thermal oxidation and can react with a number of atmospheric chemicals to produce derivatives (Ravindra et al., 2008). According to the International Agency for Research on Cancer (IARC) 48 PAHs can be carcinogenic for humans or animals, however, there are 16 most carcinogenic PAHs which are studied all over the world due to their health effects namely naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Ph), anthracene (An), fluoranthene (Fl),

pyrene (Py), benzo[a]anthracene (BaA), chrysene (Ch), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IP), dibenzo[ah]anthracene (DBA) and benzo[ghi]perylene (BghiP). The strength of their carcinogenicity grows with their molecular weight. However, it is still unknown if the carcinogenicity of PAHs (which always occur in the mixture form and never as a single compound in the air) may be ascribed to the individual hydrocarbons or if it is rather the concerted effect of some PAHs combined together (Kozielska et al., 2015).

Recently particles of size less than 1 µm (PM_1) have gained importance due to their effects on visibility degradation (Jin et al., 2006), their tendency to penetrate deeper into respiratory system and they got deposited in the alveolar region of the lung during normal breathing (Salma et al., 2002). PM_1 is composed of a large number of individual compounds such as carbonaceous (Gou et al., 2016), water soluble inorganic ions (Tao et al., 2012), major and trace metals (Trippetta et al., 2015, Talwar and Bharati, 2012), PAHs (Singh et al., 2015) etc. Among these carbonaceous aerosols are the important part in PM_1 (Cong et al., 2015, Wan et al., 2015) and it consists of organic carbon and elemental carbon. Numerous studies on carbonaceous matter in particulate matter (PM) have been carried out but few have focused on PM_1 (Kaul et al., 2011). Organic carbon is associated with the scattering of solar radiation, whereas, elemental carbon not only absorbs CO_2 and methane but also absorbs large visible and infrared light and thus contributes to the warming up of atmosphere and decrease of atmospheric visibility (Cong et al., 2013). Elemental carbon is mainly present in the sub-micron (PM_1) particles and the size of EC particles are predominantly between 0.05 and 1 µm with a life time varying from 2 to 11 days in the atmosphere (Schulz et al., 2006, Vodicka et al., 2015).

PM_1 mass is largely composed of water soluble inorganic ions (WSII) (~48.9%) (Lyu et al., 2015). The possible sources of WSII are crustal, re-suspension road dust, coal combustion and biomass burning. WSIIs play an important role in the earth's radiation balance and are also related with particle formation, growth and evaluation process (Wang et al., 2006). Among the inorganic ions sulphates, nitrate and ammonium are the major species present in PM_1 (Talwar and Bharati, 2012). Sulphate is primarily concerned with scattering of solar radiation and thus has a cooling effect on the atmosphere. Researches have also said that most of the sulphate and nitrate are exist as ammonium sulphate [$(NH_4)_2SO_4$] and

ammonium nitrate (NH_4NO_3) (Chakraborty and Gupta, 2010). The important reaction highlighting the gas phase oxidation of SO_2 and NO_2 to form gaseous acids H_2SO_4 and HNO_3 are as follows:

$$OH + SO_2 \xrightarrow{M} HOSO_2 \xrightarrow{H_2O} H_2SO_4$$

$$OH + NO_2 \xrightarrow{M} HNO_3$$

The concentration and size distribution of the trace metals are governed by the nature of emissions to the atmosphere, as well as by rates of wet and dry deposition, cloud processing, and exchange of air between the boundary layer and the free troposphere and chemical transformations. The importance of the study of metals lies in the fact that they have varying degree of toxic effects on both the health and the environment. Metals can enter in the atmosphere through variety of sources and are then passed to human systems. Metals have significant toxicological and carcinogenic effects on human health which may be either acute or chronic. They enter the respiratory tracts causing significant lung related diseases like asthma, bronchitis and may also lead to various allergies (Birmili et al., 2006).

The study of particulates is more important for their adverse health effects and their probable risk assessment. There is no ambient air quality standard for PM_1, but several epidemiological studies suggested that PM_1 can easily penetrate in the alveolar region of lungs and deposited deep in the lower respiratory tract and escape the natural clearance mechanisms of tissues (Hong et al., 2002). Most of the particulate matter consists of 90-95% of coarse particles, while, sub-micron particles (PM_1) are only 10-5% of the total mass, these particles have greater total surface area than coarse particles and studies show that particles belonging to these categories may pose great threat to human health because for the same mass, they absorb more toxic and carcinogenic compounds (Alias et al., 2007). Therefore, sub-micron (PM_1) particles although, being lesser in concentration present health threat by causing greater lung penetration and onward passage across the air-blood barrier (Kelly and Fussell, 2012). Metals are the class of atmospheric pollutants that play a key role for the determination of health effects of particulate matter. Some of the metals are known to induce formation of reactive oxygen species (ROS) and hydroxyl radical ($*OH^-$) in biological tissues, while others cause neurological disorders, different forms of cancer and

other ailments. About 70-80% of the trace metals like- cadmium, chromium and lead have been found in PM_1. PAHs are also studied in PM_1 due to their carcinogenic and mutagenic behaviour and thereby producing adverse health effects. There is still a relatively limited amount of data for the sub-micron fraction available at present. In fact, many surveys are still focusing on coarse and fine PM fractions, despite the larger potential of PM_1 to adversely affect human health (Khillare and Sarkar, 2012). As a consequence, the assessment of PM_1 levels and chemical composition and the assessment of the associated health risk have become challenging issues (Trippetta et al., 2015).

In India, studies on PM_1 are very sparse. Results have been reported from Kanpur (Singh and Gupta, 2016, Chakraborty and Gupta, 2010) and Chhattisgarh (Deshmukh et al., 2011, Deshmukh et al., 2013) only. The present study is being initiated to study PM_1 in terms of chemical composition and health risk assessment.

LITERATURE REVIEW

Atmospheric particulate matter has led to significant deterioration of the air quality in the past, and the present trends are continuing to add to the increasing pollution worldwide. A number of studies have been conducted on the characterization of particulate matter. In the past two decades majority of the studies were focused on the measurement and chemical characterization of total suspended particulates (TSP) (Fang et al., 2003, Arditsoglou and Samara, 2005, Alias et al., 2007, Satsangi et al., 2010, Deng et al., 2011, Pachauri et al., 2013, Ram et al., 2012, Boreddy and Kawamura 2015). Few studies have been conducted on characterization of ultrafine particles although there characterization is important as they are concerned with the global climatic change, health problems and visibility degradation.

Particulate matter is composed of a number of chemical constituents which include Organic Carbon (OC), Elemental Carbon (EC), metals, water soluble ions and Poly Aromatic Hydrocarbons (PAHs). Carbonaceous aerosols have been studied by various researchers and have been shown to have great impacts on the environment and health (Frazer, 2002).

Total suspended particulate (TSP) refers to all particles in the atmosphere and it was the first indicator used to represent suspended particles in the ambient air (Alias et al., 2007). In India, TSP concentration was measured in Kolkata at residential and industrial site and range was 62.4 – 401.2 and 125.7 – 732.1 $\mu g/m^3$ respectively (Gupta et al., 2007). TSP concentration in Ahmedabad at a sub-urban site was in the range 60 – 250 $\mu g/m^3$ (Rastogi and Sarin, 2009). They also determined ionic composition and carbonaceous aerosols in their study and reported that, among water soluble inorganic ions, anionic composition was dominated by SO_4^{2-} and NO_3^- whereas Ca^{2+} and NH_4^{2+} were the dominant cations. The average concentration of SO_4^{2-} and NO_3^- were 4.35 and 1.43 $\mu g/m^3$ respectively. In India, carbonaceous concentration in TSP was determined by Ram et al., 2012 at Allahabad and Hisar at urban site on clear, haze and fog events. At Allahabad the TSP concentration was 212 $\mu g/m^3$ during clear days and it was 247 and 302 $\mu g/m^3$ during haze and fog events. OC and EC concentration followed the trend fog > haze > clear days. At Hisar, the average TSP concentration was 147, 199 and 162 $\mu g/m^3$, during clear, haze and fog events and the OC-EC concentration followed the trend of highest on haze days followed by fog and clear

days. At Agra, carbonaceous concentration in TSP was measured by Satsangi et al., 2010 at a Sub-urban site reported average concentration of OC and EC to be 60.9 and 7.5 $\mu g/m^3$.

Shahsavani et al., 2011 determined water soluble inorganic ions in TSP at an urban site of Iran. Among the ions maximum concentration was found for SO_4^{2-} (33.5 $\mu g/m^3$) followed by Ca^{2+} (30.6 $\mu g/m^3$) and NO_3^- (27.5 $\mu g/m^3$). They found that water soluble ions contribute to 9.5% of TSP mass. Shen et al., 2009 determined inorganic ions in TSP during haze and normal days at a sub-urban site of China. The total ionic mass concentration in TSP during normal days was 80.1$\mu g/m^3$, represents 32.9% of total TSP mass, whereas, during haze days the total ionic mass concentration was 266.1$\mu g/m^3$ representing 39.0% of total TSP mass.

In addition to Carbonaceous and Water Soluble Inorganic Ions, metals were also studied in TSP. In Kosovo (Yugoslavia) metals were determined in TSP at three sites (traffic, near lead mine and near coal fire power station). The TSP average mass concentration was 672, 109 and 181 $\mu g/m^3$ at all three sites. The concentrations of metals for the three sites were: Cr: 58, 11 and 26 ng/m^3, Fe: 6705, 1725 and 2757 ng/m^3, Ni: 48, 10 and 18 ng/m^3, Cu: 45, 179 and 114 ng/m^3 and Pb: 176, 25 and 247 ng/m^3 (Arditsoglou and Samara, 2005). In India, Rastogi and Sarin, 2009 studied metals in TSP. The average concentrations of metals were: Fe, 450 ng/m^3; Mn, 102 ng/m^3; Pb, 117 ng/m^3; and Zn, 136 ng/m^3, respectively.

PAHs were reported in India in TSP by Sharma et al, 2007 at Delhi at a sub-urban site. The average mass concentration of PAHs determined was 668 ng/m^3. They also showed that B*(ghi)*P is the dominant species in their study having annual concentration of 100.5 ng/m^3.

PAH concentration was also determined in TSP in other countries. In Hong Kong, PAHs were determined at urban site and they range from 0.41 to 48 ng/m^3. In their study they found out main PAHs were phenanthrene, fluoranthene, pyrene, b(ghi)fluoranthene, benzo(a)anthracene, chrysene, benzo(b+k)fluoranthene, benzo(a)fluoranthene, benzo(a)pyrene (BaP) and indeno-(1,2,3-cd)pyrene (Zheng and Fang, 2000).

Later, TSP was considered too unspecific to be used as a basis for air quality standard. In July 1987, United State Environmental Protection Agency (USEPA) introduce a new term PM_{10}, which include only those particles with aerodynamic diameter less than 10µm (Alias

et al., 2007). PM_{10} and $PM_{2.5}$ both were extensively studied both in India and other countries (Kulshreshtha et al., 2010, Mishra et al., 2013, Jung et al., 2011, Deshmukh et al., 2012, Ansari, 2009, Zhamsueva et al., 2015, Sharma et al., 2006, Zhang et al., 2015, etc.)

Mass concentration, carbonaceous and ionic composition of $PM_{2.5}$ was determined by Zhang et al., 2015 in Hong Kong at a Sub-urban site during haze and non-haze episodes. The mass concentration of $PM_{2.5}$ during haze episodes was 255.0 and 136.6 μg/m^3 during non-haze episodes. The ionic concentration was highest for SO_4^{2-} 40.4 during haze and 13.5 μg/m^3 during non-haze periods followed by NO_3^- 28.5 and 9.8 μg/m^3 during haze and non-haze periods, lowest concentration was found for Mg^{2+} 0.3 and 0.2 μg/m^3 during haze and non-haze periods. The percentage composition of measured ions to $PM_{2.5}$ was 42.0% and 29.0% during haze and non-haze periods. OC and EC concentrations determined during haze periods were 43.4 and 9.5 μg/m^3 respectively and during non-haze periods concentrations of OC and EC were 27.0 and 7.0 μg/m^3. In Italy, carbonaceous aerosols in PM_{10} were studied recently for their spatial and seasonal variability at industrial, traffic, urban, semi-rural, rural and remote locations. The results showed that the OC concentrations ranged from 1.2μg/m^3 to 15.2 μg /m^3. The EC concentrations exhibited a larger variability, ranging from 0.1 μg/m^3 - 5.6 μg/m^3, and increased more than 50 times from remote to traffic sites (Sandrini et al., 2014). A long term study conducted by Ahmed et al., 2014 at a rural site in New York showed about 32% decrease in BC concentrations in 27 years and on the annual basis about 18% contribution to the emitted BC came from wood burning.

Pachauri et al., 2013 carried out their study in $PM_{2.5}$ samples collected at traffic, rural and sub-urban sites in Agra. $PM_{2.5}$ mass concentrations were reported to be higher than the NAAQS and WHO standards. The average concentrations of OC and EC at the traffic, rural and sub-urban were reported to be 86.1 ± 5.2 and 19.4 ± 2.4, 30.3 ± 12.9 and 4.0 ± 1.5 and 44.5 ± 18.5 μg/m^3 and 5.0 ± 1.4 μg/m^3 respectively.

PM_{10} and $PM_{2.5}$ were also characterized for water soluble ions. Deshmukh et al., 2012 carried out their study at urban site in Raipur in PM_{10}. The mass concentration of PM_{10} samples ranged from 109.8- 455.6 μg/m^3 and annual average concentration was 270.5 μg/m^3. The total water soluble inorganic ions annual concentration determined was 27.8 μg/m^3. The average mass concentration of PM_{10} and $PM_{2.5}$ were 219 and 97 μg/m^3 in Delhi.

Among inorganic ions SO_4^{2-} was the most dominant species in both PM_{10} and $PM_{2.5}$ with average concentration of 19.8 and 27.7 μg/m^3 in $PM_{2.5}$ and PM_{10} followed by NO_3^- which is 6.4 and 14.4 in $PM_{2.5}$ and PM_{10} (Tiwari et al., 2009).

In Xi'an, China at a sub-urban site $PM_{2.5}$ samples were analyzed for inorganic ions. The average annual concentration of ions was 45 μg/m^3 and the most abundant ions were SO_4^{2-}, NO_3^- and NH_4^+ (Shen et al., 2012).

In addition to carbonaceous aerosols and ions, metals were also detected in PM_{10} and $PM_{2.5}$. In a study reported from Lucknow in PM_{10} at 10 different sites; 4 residential, 5 commercial and 1 industrial, the average concentrations of metals at the 10 sites were 232.1, 179.0, 297.3 and 218.4 ng/m^3 at residential sites, 254.4, 281.0, 254.0, 210.5 and 424.0 ng/m^3 at commercial sites and 169.5 ng/m^3 at industrial site (Sharma et al., 2006).

Wang et al., 2006 reported $PM_{2.5}$ and PM_{10} at four sites (semi-rural, industrial, commercial and traffic site) and average mass concentration varied from 90 - 105 μg/m^3 in $PM_{2.5}$ and 138 – 152 μg/m^3 in PM_{10}. Similarly, the average concentration of OC varied from 29 – 37 μg/m^3 and EC concentration varied from 9 - 17 μg/m^3 in $PM_{2.5}$ and the average concentration of OC varied from 34.8 – 39 μg/m^3 and EC concentration varied from 10 – 19.8 μg/m^3 in PM_{10} in all four sites. Among inorganic ions, SO_4^{2-} was the dominating species and concentration varied from 26.5 – 42.7 in $PM_{2.5}$ and 27.6 – 43.7 μg/m^3 in PM_{10} in all four sites. Among metals, Ca had the highest concentration at semi-rural site in $PM_{2.5}$ as well as PM_{10} (1.2 and 3.5 μg/m^3). At industrial site K has the maximum concentration in $PM_{2.5}$ 2.0 μg/m^3 and Al has highest concentration in PM_{10} 5.0 μg/m^3. At commercial site also Al has highest concentration in PM_{10} 8.0 μg/m^3 and K has highest concentration in $PM_{2.5}$ 2.7 μg/m^3.

In China, Li et al., 2015 reported health risk assessment study at two sites; sub-urban and commercial and found that non-carcinogenic health risk for children and adults because of As, Cd, Cr, Mn and Ni were at safe level of 1 at both sub-urban and commercial site.

Health effect of $PM_{2.5}$ was measured by Khillare and Sarkar, 2012 in Delhi and they report the incremental life time cancer risk (ILCR) assessment shows that upto 2908 excess cancer cases (102 for Cd, 2559 for Cr(VI) and 247 for Ni) were likely to be there due to lifetime inhalation exposure to these species (Cd, Cr (VI) and Ni). Mutagenicity assessment of PAHs has also been reported from Agra at a sub-urban site in $PM_{2.5}$ using *Salmonella*

typhimurium strains TA98 and TA100 both with and without S9 mix. The results shows the direct acting mutagenicity obtained with TA98 ranged from 285 - 935 rev/m^3 with an average value of 594±1.4 rev/m^3. Direct mutagenic activity detected in the TA100 strains ranged from 343 to 1220 rev/m^3 (Average value 834±1.4 rev/m^3) without S9 and 467 to 1866 rev/m^3 (Average value 1195±1.5 rev/m^3) with S9 and a higher potential for base pair mutagenicity was observed as compared to frame shift mutagenicity due to greater mutagenic response towards TA100 (Dubey et al., 2015).

The current interest of scientific and regulatory communities is moving to fine fractions i.e. PM_1 due to their relevant implications on the human health (Tsiouri et al., 2015). Like Total Suspended Particulates, PM_{10} and $PM_{2.5}$, PM_1 is also characterized for Carbonaceous aerosols, Water Soluble Inorganic Ions (WSII), metals and PAHs. The studies on chemical characterization of PM_1 were mostly from outside India (Li and Lin, 2002, Lin and Lee, 2004 Ariola et al., 2006, Decesari et al., 2010, Onat et al., 2013, Halek et al., 2014, Pateraki et al., 2014, Titos et al., 2014, Valotto et al., 2014, Wiseman et al., 2014, Sarti et al., 2015). The average mass concentration of PM_1 was determined in Lithuania at Rūgšteliškis at three different sites (two background and one urban) the average mass concentration was 7.7 µg/m^3 at urban, while concentrations were 4.2 and 3.4 at the background sites (Meinore et al., 2014). Organic and Elemental carbon was determined in $PM_{1.0}$ at Japan and the results reported that the concentration of organic carbon ranged from 0.41 to 2.49 µg/m^3 and the average concentration was 1.2 µg/m^3 and for elemental carbon the concentration ranged from 0 to 0.85 with an average concentration of 0.36 µg/m^3, respectively (Kunwar et al., 2015). Elemental Carbon (EC) concentrations have been determined in $PM_{1.0}$ at a sub-urban site in China and EC concentration varied from 1.10 to 15.27µg/m^3. The average concentration of PM_1 and EC in winter were 112.78±42.77 µg/m^3 and 8.06±3.16 µg/m^3 and in summer were 40.52±22.53 and 1.95±0.53 µg/m^3 respectively (Gou et al., 2016). In another study from China (Guangzhou) at an urban site Carbonaceous aerosols and inorganic ions have been measured and the annual mean concentration of OC and EC in PM_1 were 6.2±3.5 µg/m^3 and 5.0±2.9 µg/m^3, respectively and the Total Carbon (TC) accounted for 23.0±4.4% of PM_1 by mass. The annual average value of total water-soluble ionic species accounted for 43.2±7.7% of PM_1 mass (Tao et al., 2012).

Ionic composition was also determined in China during haze and non-haze days (Cheng et al., 2014) and the average concentrations were 56.70±23.20 and 58.32±23.95 μg/m^3 at commercial and sub-urban site, respectively. Ions accounted for 48.4% and 47.4% of $PM_{1.0}$ mass at the commercial and sub-urban site. In Italy, metals were studied by Trippetta et al., 2015 from April 2009 to March 2010 at an industrial site in PM_1. Their results also showed that trace elements accounts for 23.3% of PM_1 mass. Health risk assessment was also done by them and they report that non-carcinogenic effects due to the exposure to Al, Cd, Cr, Mn and Ni in PM_1 were not significant, whereas, cancer risk associated with Cd, Cr, Ni ad Pb in PM_1 was acceptable.

Studies on PM_1 have been mainly reported by Chakraborty and Gupta, 2009 and Deshmukh et al., 2011 in India. Ionic composition was determined at Kanpur during monsoon and post-monsoon. The average mass concentration during monsoon was 30.03μg/m^3 and during post- monsoon 63.75μg/m^3 (Chakraborty and Gupta, 2009). Another study was conducted at Chhattisgarh during 2009 to 2010 and the concentration of $PM_{1.0}$ mass ranged from 8.6-134.7 μg/m^3 and the mean annual concentration was 64.7±36.9 μg/m^3. The concentration of total soluble inorganic ions in PM_1 accounted for 16.98% of the total PM_1 mass (Deshmukh et al., 2011). In Kanpur, Rajput et al., 2015 reported water soluble inorganic ions and metals contributed about 50% to PM_1 and rest mass is from carbonaceous species.

Singh et al., 2015 detected Polycyclic Aromatic Hydrocarbons (PAHs) in PM_1 at Kanpur. In their study they report 16 PAHs in which 14 are demarcated by USEPA as priority pollutants. Naphthalene showed lowest concentration of (4.04 ng/m^3) and fluoranthene showed highest concentration of (124.26 ng/m^3). Another study on PAHs was conducted at a sub-urban site of Kanpur during Foggy days on PM_1. The PAHs average mass concentration was 529.17±24.87 ng/m^3. The lowest concentration of PAHs was reported for naphthalene (3.76 ng/m^3) and the highest was for fluoranthene (97.53 ng/m^3) (Singh and Gupta, 2016).

OBJECTIVES

The primary particulate matter which is emitted directly into the atmosphere comprises mainly of sub- micron (PM_1) particles. Exposure to PM_1 is of interest due to their acute and chronic effects on human health. Only one study Singh and Gupta, 2016 reported health risk assessment of PM_1 at Kanpur.

There is limited information in the literature on mass concentrations, physico-chemical analyses and the hazard analyses of the PM_1 present in the ambient air. In lieu of the importance of PM_1 in health the present study is proposed to chemically characterize and evaluate health risk of PM_1 at two sites of Agra which lies in Indo Gangetic Plain (IGP), the most populated region of North Central India. The objectives of the study are:

A. To investigate the distribution of particle mass and particle components, such as:

- Major anions (F^-, Cl^-, NO_3^- and SO_4^{2-}) and major cations (Ca^{2+}, Mg^{2+}, Na^+, K^+).
- Trace metals (Fe, Ni, Cd, Cu, Cr, Zn, Mn and Pb).
- Polycyclic Aromatic Hydrocarbons.

B. To carry out source apportionment of PM_1 components

C. To evaluate human health risk assessment of trace metals and PAHs in $PM_{1.}$

METHODOLOGY

Site Description

The city of Agra is situated in the north central region of India (27°10′ N, 78° 32′E, and 169 m.s.l.) with two-thirds of its peripheral boundaries (SE, W and NW) being surrounded by the Thar desert of Rajasthan. It is a semi-arid region characterized by loose, sand, calcareous soil and a distinct monsoon season. The climate of Agra is hot and dry during the summer with a relative humidity of 25% to 40% and the temperature ranging from 25°C to 46° C, while the winter season features a cold weather with a relative humidity of 60% to 90% and low temperature ranging between 0.6°C and 22°C. The annual rainfall in Agra is about 650 mm and the winds usually come from west and north-west directions. Sampling will be carried out at two sites:

a) Campus Site: Sampling will be carried out on the roof top of Science Faculty building at Dayalbagh Educational Institute (DEI) located at Dayalbagh, Agra. DEI is a suburban site surrounded by a small residential community and agricultural fields and the industrial sector of Agra is about 10 km away. The institute lies by the side of the road with a vehicular density of about 1000 vehicles per day. The population around the area is about 25,000. The National Highway, NH-2 lies about 2 km from the sampling site. Both, Mathura oil refinery and Firozabad glass industry are located about 40 km from Agra.

b) Traffic site: Sampling will be carried out at a building situated about 50 m from National Highway, NH-2. National Highway-2 or NH-2 commonly referred as Delhi–Kolkata Road, is a busy National Highway where traffic density is about 10^6.

Sample Collection and Measurement

PM_1 samples will be collected for 24 hour on a pre-weighed 47 mm PTFE filters using a PM_1 Particulate Sampler (Envirotech APM 577) at a flow rate of 10 lpm. Before exposure, the PTFE filters heated in a muffle furnace at 900°C for 4 hours to remove organic impurities. Before and after sampling the filter papers will be kept in desiccator for 24 hours and then weighed on an electronic microbalance (Mettler) to determine the PM mass. After weighing the samples will be wrapped in aluminium foil and then sealed in

polyethylene zip lock bags and stored in deep freezer at -4°C until the time of chemical analysis to prevent the evaporation of volatile compounds.

Analysis

Ion Analysis

The water soluble inorganic ions (cations and anions) will be determined using Dionex ICS 1100 Ion Chromatograph system (Dionex corp, Sunnyvale, CA). For cation analysis, filter paper will be extracted by sonicated with De Ionized water for 45 min and analysis will be performed using 20 mM Methane Sulphonic Acid as an eluent for Na^+, K^+, Mg^{2+} and Ca^{2+}. The system will be equipped with guard column (CG12A), analytical column (CS12A) and cation self-regenerating suppressor (CSRS 300 4 mm). The anions will be extracted using DI water and the system will be equipped with guard column (AS11A), analytical column (AS11) and anion self-regenerating suppressor (ASRS-ULTRA 4 mm), 6 mM NaOH will be used as a eluent for Cl^-, NO_3^- and SO_4^{2-}. Blank corrections will be made using similar process.

Analysis of Metals

Metals will be analyzed using Atomic absorption Spectroscopy (AAS). After sampling, the filter paper will be placed in 100ml Teflon beakers, previously soaked in 20% (v/v) HNO_3 for 4 hours and rinsed thoroughly with De Ionized water. 3 ml of HNO_3 will then be added and the beakers will be covered with watch glass. The contents will be heated on a hot plate in a fume hood. The digestion of the samples will be continued until the acid nearly evaporates. The beakers and the watch glass will be allowed to cool. 2 ml HNO_3 will then be added and heating continued again to near dryness. 1 ml of hydrofluoric acid will then be used to dissolve any particles present followed by gentle heating near to dryness. This dissolves the filter paper and all solid material. The dissolved sample will be cooled and about 10 ml De Ionized water will be added. The sample will be transferred to 25 ml volumetric flasks and the volume made up with acidified De Ionized water (1% HCl and 0.7% HNO_3) before filtering to remove silicates and other insoluble materials. Finally, the samples will be placed in plastic containers and stored in a refrigerator at 4°C until analysis.

Analysis will then be made using AAS of the make Lab India, AA 8000 and equipped with hollow cathode lamps.

Analysis of PAHs

After sampling, one-fourth of the filter papers will be cut into small pieces and extracted using 150 ml Dichloromethane (DCM) by ultra sonication. After that the extracts will be filtered and concentrated using rotavapor at a bath temperature of ≤40°C. The extract will be cleaned employing a silica gel column of 15 cm length and 1.5 cm diameter. To remove the interference of aliphatic hydrocarbons the column will be first eluted by 50 ml of hexane followed by a second elution by DCM: hexane (1:1). This fraction containing the PAHs will be again concentrated by rotary evaporation. The samples will be stored in glass vials wrapped in aluminium foil at low temperature until analysis.

PAHs will analyzed in the split less mode using a temperature gradient program by Gas Chromatograph (GC, Shimadzu 17AATF, version 3.0) equipped with a Flame Ionization Detector (FID) and capillary column (25 m length, 0.3 mm internal diameter: BP) with dimethyl poly siloxane as stationary phase. Nitrogen will be the carrier gas at a flow rate of 12.7 ml/min. The oven temperature will be held at 40 °C for 5 min and programmed to rise to 179 °C at 10 °C min^{-1}, held for 2 min and then elevated to 300 °C at 9 °C min^{-1}. The temperature of injector and detector will be maintained at 210 and 310 °C respectively with a total run of 40 min.

Health risk assessment

Life time average daily dose (LadD) is the amount of intake per kg of body weight per day of a chemical suspected of having adverse health effects when absorbed into the body over a long period of time. Hazard quotient or non-carcinogenic health effects will be assessed by dividing a LadD (life average daily dose) of each element for an inhalation pathway by the corresponding reference dose (RfD) or a ratio of an exposure to a reference value. For carcinogens, LadD will be multiplied by the corresponding cancer slope factor (CSF) to yield the cancer risk.

$$LadD\ (mg\ kg^{-1}\ day^{-1}) = (Cm \times Ir \times Cf \times Ef \times Ed)/\ (Bw \times At)$$

$$Hq = LadD/RfD$$

$$IlcR = LadD \times CSF$$

where Cm is the concentrations of metals (μg m^{-3}) calculated per day (24 h), in air particles, Ir is the air inhalation rate (10 m^3 day^{-1} for child and 20 m^3 day^{-1} for adult), Cf is the unit conversion factor (0.001), (Ef) is the exposure frequency (350 days/years for both child and adult) and (Ed) is the exposure duration (6 years for child and 24 years for adult). Ef of 350 days per year is used to calculate the lifetime exposure of human receptors (both child and adult) with the assumption that the receptors in each exposure scenario are exposed to all of the scenario-specific exposure pathways 350 days per year. (Bw) is the body weight (15 kg for child and 70 kg for adult), (At) is the averaging time for carcinogens (25,550 days for both child and adult), and (CSF) is the cancer slope factor (per mg kg^{-1} day^{-1}).

The reference dose (RfD) is a measurement of the highest permissible risk on the human population through daily exposure taking into consideration of a sensitive group during a lifetime The doorway of the RfD value can be used to suggest whether there is an inauspicious health effect during a life time. If the LadD value is lower than the reference dose, it is indicated that there would not be any adverse health effect; otherwise if the LadD value is higher than the Rfd, it is likely that the exposure pathway will cause an adverse human health effect.

For a monitored combination of chemicals, an indication of risk of toxic effects from an inhalation exposure HI can be used. Its formula is

$$Hi = \sum Hq:$$

Hi refers to the "sum of more than one Hazard Quotient for multiple substances." Hi is equal to the sum of Hq and represents the total risk of a non-carcinogenic for multiple elements. If the value of Hi $\leq$ 1, it is considered that there is no significant risk of non-carcinogenic effects. If Hi >1, it means there is a higher probability of adverse health effects, and the possibility of adverse effects increases with the increasing value of Hi.

Mutagenicity assay

Mutagenicity assay will be conducted by the Ames test (Maron and Ames, 1983). Two tester strains of *Salmonella typhimurium* (his-) TA100 and TA98 will be used for base-pair mutation and frame shift mutation, respectively. For performing Ames test, the organic

extracts of sampled PAHs will be re-dissolved in DMSO in fixed ratio immediately before use. The bacterial strains will be initially cultured in cultured tubes containing beef extract agar medium, 15-18 hour before the experiment. The test will be performed in plates containing 2 layers of agar in which the bottom agar (1.5%) will provides a suitable support media and the top agar (0.07%) will be for applying the test chemical and the desired strain. Vogel-Bonner minimal media E (50x) supplemented with agar and glucose will be used as bottom agar. Two ml of the top agar consists of agar, NaCl and histidine/biotin. The extracts will be applied to the plate at dose levels of 10,20,40,60 and 80 µl/ plate. 20 µl per plate metabolizing enzyme (rat liver extract i.e. S9) will be used for determining the indirect mutagenic activity. In addition to the test plates, a negative control consisting of DMSO (100 µl) solvent blank will be used to establish the number of colonies that will arise spontaneously for each of the tester strains. The plates will be incubated at 37°C for 63 h in dark in inverted position and subsequently the reverted colonies formed in each plate will be counted. Counting will be performed using a handheld digital colony counter (LA 663, Himedia). Mutagenic response will be classified as positive if a reproducible dose-dependent increase of the number of reverted colonies over and above those in the negative control will observed (McDonald and Spears, 1998), Mutagenic activity will be calculated from positive slope of the dose-response curve calculated by the least square linear regression.

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